Efficient evolution of reactive oxygen species over the coordinated π-delocalization g-C$_3$N$_4$ with favorable charge transfer for sustainable pollutant elimination

Jingjie Liu[a,1], Chuanbao Xiong[a,b,1], Shujuan Jiang[a,b,*], Xi Wu[a,b], Shaoqing Song[a,b,*]

[a] *Laboratory of Atmospheric Environment, Key Laboratory of Nuclear Resources and Environment (State), East China University of Technology, 418 Guanglan Road, Nanchang 330013, PR China*
[b] *School of Materials Science and Chemical Engineering, Ningbo University, 818 Fenghua Road, Ningbo 315211, PR China*

A B S T R A C T

Reactive oxygen species (ROS) as efficient and green oxidants can be generated through various catalytic methods, which is important for environmental chemistry and chemical engineering. Here we construct an efficient photocatalytic system to evolve ROS for environmental purification. In the work, the coordinated g-C$_3$N$_4$ photocatalysts (Cu/C$_3$N$_4$) are designed by interacting N 2p lone electrons at vacancy site of tri-s-triazine polymer with 3d orbits of Cu^{2+}, resulting in the extended π-delocalization structure of g-C$_3$N$_4$. Experimental and theoretical calculations confirm that the extended π-delocalization structure of Cu/C$_3$N$_4$ strengthens the light capturing capability from ultraviolet to near infrared light, favors the charge transfer from N 2p of C$_3$-N to the linked C, and Cu atoms. As a result, the efficient evolution of ROS including O$_2^-$ (13 μmol L^{-1} h^{-1}), and H$_2$O$_2$ (550 μmol L^{-1} h^{-1}) can be completed over Cu/C$_3$N$_4$ photocatalysts. Cu/C$_3$N$_4$ photocatalysts results in a highly efficient generation of ROS and also exhibited a sustainable removal efficiency for NO, and HCHO, which demonstrates a promising application in the field of environmental purification.

1. Introduction

Reactive oxygen species (ROS), such as ˙O$_2^-$, ˙OH, and H$_2$O$_2$, as highly efficient and green oxidants, are of great importance for environmental chemistry and chemical engineering [1,2]. Currently, these reactive oxygen species can be photocatalytically yielded by O$_2$ activation over semiconductor-based photocatalysts under irradiation [3,4]. In the photocatalytic procedure, photo-excited electron (e$^-$) activates and reduces O$_2$ into ˙O$_2^-$, and hole (h$^+$) oxidizes H$_2$O into ˙OH and/or O$_2$ [5,6]. With the in-depth study of photocatalysis theory, numerous types of semiconductor-based photocatalysts, e.g., Ag$_3$PO$_4$@CoFe$_2$O$_4$ [7], TiO$_2$/C-Dots [8], CuO-SiO$_2$ [9], AgVO$_3$/MoS$_2$ [10], AgBiO$_3$ [11], and Ag$_3$PO$_4$ [12] have been utilized to photocatalytically activate O$_2$ for yielding oxygen active species. Thermodynamically, it is relatively difficult for one-electron reduction of O$_2$ to ˙O$_2^-$ (−0.33 V) compared with multi-electron reduction (+0.69 V for O$_2$/H$_2$O$_2$, and +1.23 V for O$_2$/H$_2$O, respectively) [13]. Kinetically, the photocatalytic reactions between photon-generated carriers and

reactants require several microseconds, however, e$^-$ recombines h$^+$ from several picoseconds to dozens of nanoseconds [14], resulting in quenching and thus restricting O$_2$ activation [15,16]. Therefore, O$_2$ chemical adsorption, and efficient e- transfer illustrates a crucial role in the photocatalytic activation and reduction of O$_2$ [17].

g-C$_3$N$_4$, the π-delocalization tri-s-triazine polymeric compound made up of C and N, has been confirmed to be a visible-light-excited photocatalyst [18–20], and its conduction band potential is −1.23 V versus NHE (pH = 7) [21–23], which is much lower in comparison with potentials of O$_2$/˙O$_2^-$ (−0.33 V), O$_2$/H$_2$O$_2$ (+0.69 V), and O$_2$/H$_2$O (+1.23 V). As a result, g-C$_3$N$_4$ can usually be used to photocatalytically evolve active oxygen species [24–30]. For instance, Wang et al. constructed the black phosphorus (BP)/g-C$_3$N$_4$ heterostructure photocatalyst for O$_2$ activation and reduction [13]. The heterostructure strengthens visible-light absorption, facilitates charge transfer, and increases the efficiency for the evolution of ˙O$_2^-$ and H$_2$O$_2$; We designed solid-solution-like o-C$_3$N$_4$/Ag$_2$SO$_4$ photocatalyst as an efficient photocatalytic system for synthesizing ˙O$_2^-$, ˙OH, and H$_2$O$_2$ [6]. Dong and

Wang et al. reported that H_2O_2 evolution efficiency was promoted over Z-scheme g-C_3N_4/perylene imides [31]. Moreover, the photocatalytic rate for H_2O_2 evolution was distinctly enhanced over g-C_3N_4 with SiW_{11} as cocatalysts [32]. Nevertheless, photocatalytic efficiency over g-C_3N_4 always suffers from two shortcomings. One is the existence of vacancy structure in the tri-s-triazine polymer, and the other is the large electronegativity difference between C and N [33–35]. The former directly leads to increase the recombination probability of e^- and h^+, and the latter induces the existence of abundant hydrogen bonding in the π-conjugated tri-s-triazine polymer [36,37]. The hydrogen bonding promotes the superposition of the polymer nanosheets, thus hindering the transfer of e^- within the layers of the delocalized tri-s-triazine nanosheets [36]. Orbit theory calculation reveals isolated electron of N p_z orbital at vacancy sites. In accordance with the coordination field theory, N lone electron may coordinate vacant p and/or d orbital of metal with the aid of static coulomb effect [6], resulting in patching the vacancy structure of g-C_3N_4 and thus extending π-conjugated system. The so-constructed g-C_3N_4 with the extended π-conjugated structure will optimize efficient electron transfer. Coordination between metal ion and N induces the charge redistribution of g-C_3N_4, which can improve the electronegativity difference between C and N. Moreover, lone electrons of O_2 will bond with d orbital of metal, and electrons from d orbital of metal will fill into anti-bonding π^* of O_2, which facilitates O_2 adsorption and activation.

Accordingly, we report an extended π-conjugated g-C_3N_4 synthesized by coordinating between Cu^{2+} 3d orbit and N $2p_z$ of tri-s-triazine polymer for efficient evolution of ROS. Experimental and DFT results confirm that charge of g-C_3N_4 is redistributed and optimized, reflecting as the slight electronegativity difference between C and N, and charge distribution uniformity because of Cu coordination. The extended π-delocalization tri-s-triazine polymer favors adsorption and activation of O_2 and H_2O. Besides, the strengthened light absorption from UV to visible and even near infrared, and the optimized electron migration are achieved on the extended π-conjugated g-C_3N_4. The extended π-conjugated g-C_3N_4 photocatalyst shows high performance for producing $^{\cdot}O_2^-$ and H_2O_2 species, which supplies ideas for designing active photocatalysts toward solar energy conversion and environmental purification.

2. Experimental

2.1. Synthesis of the extended π-conjugated g-C_3N_4 samples

The extended π-conjugated g-C_3N_4 samples were synthesized by thermally polymerizing the homogeneous mixture of carbamide and $Cu_2(CH_3COO)_4$. In the procedure, 10 g carbamide was dissolved into $Cu_2(CH_3COO)_4$ solution (25 mL, 2 mM) and magnetically stirred for 180 min. The homogeneous mixture solution was subsequently heated and stirred at 60 °C until sticky-like sample was formed. The sticky-like sample was placed in muffle furnace, and the sample was thermally polymerized at 540 °C with rate of 5 °C min^{-1} for 120 min. After natural cooling, the extended π-conjugated g-C_3N_4 sample was obtained and labeled as Cu/C_3N_4-1. In order to probe the universality of the method, Cu/C_3N_4-2 (25 mL, 4 mM), and Cu/C_3N_4-3 (25 mL, 6 mM) samples were synthesized with using the method of Cu/C_3N_4-1, respectively. In the meantime, g-C_3N_4 was directly synthesized by thermally polymerizing carbamide at 540 °C for 120 min.

2.2. Characterization

Component, crystal structure and chemical valences were tested with using X ray diffraction spectroscopy (Bruker, D8 advance), X ray photo-electron energy spectrum (ESCALAB250xi, Thermon Scientific), and IR Affinity-1 FTIR spectrometer (Shimadzu, Japan). Pattern was surveyed by field-emission-scanning-electron microscope (Hitachi), and transmission-electron microscopy (JEM-2010HR). Cu content was

detected with ICP-AES method on a Perkin-Elmer Optima 4300DV instrument. Brunauer-Emmett-Teller (BET) specific surface area was examined with using N_2 adsorption-desorption method on a Micromeritics ASAP 2020 instrument. Mott-Schottky data, electrochemical-impedance spectra and transient photo-current signals were achieved on electrochemical-workstation (660C Chenhua Instruments) with using Na_2SO_4 and KNO_3 as electrolyte solutions. Electron-paramagnetic resonances were achieved on MEX-nano, Bruker. Surface photovoltage spectra were detected by changing the potential barriers of the electrode surface in the light or dark on the home-built apparatus. Time-resolved-photo-luminescence spectrum was completed on FLS920 fluorescence-lifetime spectrophotometer (Edinburgh).

2.3. DFT calculations

DFT calculations were performed by utilizing Gaussian 09 suite of computational programs. The hybrid-density-functional B3LYP was carried out. Geometry was optimized by 6-31G(d) basis sets on the nonmetal atoms and LANL2DZ effective core-potential on Cu. Mulliken-charge distributions of geometry were achieved at the level of B3LYP/ [6-31G(d) + LANL2DZ].

2.4. Yield of ROS

ROS were detected with using EPR method. In the procedure, 10 mg Cu/C_3N_4 sample was dispersed into DMPO solution ((3.85% volume ratio, 1.04 mL including 1 mL CH_3OH). After sample was illuminated for 2 min with using xenon lamp (350 W), and DMPO-$^{\cdot}O_2^-$ was examined with EPR instrument. When H_2O was replaced with CH_3OH, DMPO-$^{\cdot}OH$ signals were detected. Photocatalytic yield of $^{\cdot}O_2^-$ was calculated by nitroblue-tetrazolium absorbance intensity (NBT) at 260 nm. In the light of 1:4 (molar ratio), yield amount of $^{\cdot}O_2^-$ was determined.

H_2O_2 evolution over Cu/C_3N_4 was also studied. 60 mg sample was dispersed into Schlenk flask (9.1% volume percent, aqueous IPA solution, 33 mL). we injected O_2 into the aqueous IPA solution for 60 min in dark, and the photocatalytic system was irradiated 300 W Xe Lamp. H_2O_2 amount was measure by titration method with the acidic $KMnO_4$ (0.2 mmol L^{-1}) as titrant, and the amount of the reacted $KMnO_4$ was the equal of H_2O_2 evolution [13].

2.5. Photocatalytic elimination of HCHO and NO

HCHO elimination was carried out in 6 L quartz reactor at 25 °C under illumination. The reactor was vertically beamed through a Xe lamp (300 W) with a UV cutoff filter (420 nm). In accordance with our previous report [38], 0.1 g thin film of Cu/C_3N_4 was prepared and installed to reaction generator. Typically, 0.1 Cu/C_3N_4 sample was uniformly dispersed into the deionized H_2O (15 mL) in a petri dish (7.0 cm d.) by ultrasonication for 25 min. The dispersed Cu/C_3N_4 was dried at 60 °C for 1 h, obtaining thin film of Cu/C_3N_4 on petri dish. Soon afterwards, the petri dish with the thin film was placed into the quartz reactor. Some volume of HCHO (38%) was imported to the reactor. After an adsorption/desorption balance in the darkness, initial content of HCHO was always maintained at ~200 ppm for each test. Under visible-light irradiation, HCHO, CO_2, and H_2O content was *in-situ* detected on a Photoacoustic IR multi-gas monitor. Meanwhile, the photocatalytic removal of NO gas was performed in the same photocatalytic system of HCHO elimination with using 600 ppb NO instead of 200 ppm HCHO. The content of NO was on-line surveyed with chemiluminescence NO analyzer. The removal efficiency (Y) of HCHO, and/or NO was evaluated in light of our previous report [39].
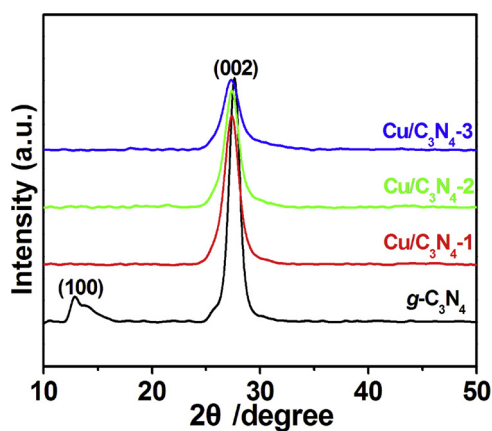
Fig. 1. XRD patterns of g-C_3N_4 and Cu/C_3N_4 samples.

3. Results and discussion

3.1. Crystal composite and morphology

In Fig. 1, it is observed that XRD pattern of g-C_3N_4 demonstrates the crystal diffraction characteristics of conjugated tri-s-triazine polymer, i.e., the pattern peak at 13.1° for diffraction plane of (100), and 27.3° for (002) [40–42]. The former plane represents the in-plane repetitive structure of tri-triazine, and the latter plane reflects the inter-layer stacking of the conjugated tri-s-triazine nanosheet [43,44]. For Cu/C_3N_4 samples, it is seen that the diffraction signal at 13.1° almost vanishes, indicating that the in-plane repetitive structure of tri-triazine has been reduced, and the vacancy defect has been compensated [45–47]. Moreover, in comparison with the diffraction peak at 27.6° for g-C_3N_4, the peak of Cu/C_3N_4 sample presents a obvious shift to 27.2°. In light of Bragg equation, inter-layer spacing is enlarged from 0.322 to 0.327 nm when Cu is introduced and coordinates with N of its vacancy structure. Additionally, it is observed that half peak width increases for Cu/C_3N_4 samples, indicating the smaller grain size for Cu/C_3N_4 samples compared with that of g-C_3N_4. The unoccupied orbits of Cu^{2+} interact with the N $2p_z$ electrons of N at vacancy structure, which in certain degree inhibits hydrogen from bonding with N. Therefore, the Cu-coordinated N of tri-s-triazine nanosheet may inhibit the superposition of g-C_3N_4 nanosheets [36,48], which results in the increase of interval spacing.

Then, the surface-chemical constituents, and their valences were examined by XPS. In the XPS spectra, the bound energies for all chemical components are calibrated on the basis of C 1s at 284.8 eV. In Fig. 2A, Cu $2p_{3/2}$ signals of Cu/C_3N_4 are observed at 932.1 eV, which are deservedly identified to be characteristic of Cu−N [49]. In Fig. 2B, O 1s signals for all samples g-C_3N_4 demonstrate the two classified peaks at 532.7 and 531.6 eV, which can be considered as $(CN)_n$-O and the adsorbed −OH species [6,50]. In Fig. 2C, N 1s spectra of g-C_3N_4 and Cu/C_3N_4 samples are fitted into C=N−C (398.4 eV), C_3-N and Cu-N (399.9 eV), and N−H (401.2 eV), respectively [39,43,51,52]. For Cu/C_3N_4 samples, peak intensity of N−H species decreases, indicating the decrease of hydrogen bonding on the Cu/C_3N_4 sample may weaken the superposition of g-C_3N_4 nanosheets. C 1s signals for g-C_3N_4 and Cu/C_3N_4 are presented in Fig. 2D. The content of Cu in Cu/C_3N_4 samples is 0.18 (Cu/C_3N_4-1), 0.33 (Cu/C_3N_4-2), and 0.53 wt.% (Cu/C_3N_4-3) as detected by ICP-AES.

The chemical compositions and structures of Cu/C_3N_4 samples were further detected by FT-IR spectra. In Fig. 3, all spectra demonstrate a clear signal at 810 cm^{-1} which is the breathing mode of tri-s-triazine [50]. Signals at 1200–1700 cm^{-1} ascribe to the vibration modes of C−N bonds in tri-s-triazine [53]. Furthermore, absorption at 3000–3400 cm^{-1} belongs to the vibration mode of N−H bonds [50]. The FT-IR spectra results suggest that Cu coordination has not break the π-conjugated structure of tri-s-triazine polymer.

Cu-coordination influence on the image of Cu/C_3N_4 has been probed through FESEM and TEM, and these results are demonstrated in Fig. 4A and B, and Fig. S1 of Supplementary data. Cu/C_3N_4 samples present grenadine-like nanolayers with enormously smooth and fluffy-flocculation characteristic, while g-C_3N_4 is made up of the accumulated and compact particles (Fig. S1). The fluffy-flocculation layers for Cu/C_3N_4 was further characterized by FESEM-EDX (Fig. 4C–F), and EDX element mappings suggest a uniform of C, N, Cu, and O for Cu/C_3N_4 sample. The grenadine-like layers with smooth and fluffy-flocculation characteristic supplies abundant reactive site and a large smooth surface for light trapping.

3.2. Microstructures and surface physicochemical properties

Nitrogen adsorption/desorption isothermal curves and the deduced pore properties of g-C_3N_4, and Cu/C_3N_4 are presented in Fig. 5A and B. All tests display type-IV isothermal curves with H3-hysteresis loops, suggesting the trait of slit-like mesopores [54]. On the one hand, Cu coordination with g-C_3N_4 leads to the expanded π-conjugated structure by "*patching*" the vacancy of tri-s-triazine; on the other hand, interlayer spacing is enlarged. In comparison with g-C_3N_4, Cu/C_3N_4 samples show much higher adsorption quantity. BET specific surface areas are 45 (Cu/C_3N_4-1), 87 (Cu/C_3N_4-2), and 138 $m^2 g^{-1}$ (Cu/C_3N_4-3), which is 1.8, 3.48, and 5.52 times that of g-C_3N_4 (25 $m^2 g^{-1}$), respectively. Pore size by calculating by BJH method is 10–15 nm for g-C_3N_4, and Cu/C_3N_4 samples, nevertheless, Cu/C_3N_4 samples demonstrate larger pore volumes. The elaborate data of these physicochemical properties for all samples are shown in Table S1. The enlarged BET specific surface areas and pore volumes are beneficial to the adsorption of the reactants and the capture of light.

3.3. DFT calculation for electronic structure of Cu/C_3N_4

DFT calculations were performed to examine Cu coordination effect on the geometry of g-C_3N_4. Fig. 6A presents an optimization process of Cu/C_3N_4 geometry by Cu^{2+} coordination with different site of conjugated tri-s-triazine. When the vacant orbit of Cu^{2+} coordinates with electron of graphic-like N in g-C_3N_4 (at site 1), the total energy is −2200.38 (Hartree). For the coordination at site 2, and 3, total energy declines to −2200.41, and −2200.43 (Hartree), respectively; it is noted that vacant orbits of Cu^{2+} spontaneously coordinate with six sp^2-hybridized N at vacancy of g-C_3N_4 (at site 4), and the total energy reduces to −2200.48 (Hartree). In this case, d-π conjugation is formed by partial π electron cloud on the conjugated tri-s-triazine ring entering into the 3d orbit of Cu^{2+}, which makes Cu^{2+} to bond with the the conjugated tri-s-triazine firmly [55,56]. Therefore, it is clearly seen that the site 4 is thermodynamically advantageous for the coordination between Cu^{2+} and six sp^2-hybridized N atoms at vacancy of g-C_3N_4, resulting in patching vacancy and thus expanding the conjugated structure. Mülliken charge analysis was used to investigate the charge distribution over g-C_3N_4 before and after coordination of Cu^{2+} with sp^2-hybridized N atoms at vacancy of tri-s-triazine nanosheet (Figs. 6B and S3). In Fig. 6B, it is seen that the difference between N and C atom around the Cu atom becomes smaller, and the distribution of electrons tends to be uniform, and electrons are preferentially concentrated around Cu, and C (linked with N of vacancy), suggesting that the effective-directional transfer of electrons is achieved over the expanded π-conjugated structure of Cu/C_3N_4 sample. N $2p_z$ orbitals of six sp^2-hybridized N atoms at vacancy sites overlap the unoccupied orbitals of Cu^{2+} (Fig. 6C), which will result in the efficient transfer of charge over Cu/C_3N_4. Moreover, the charge migration between adjacent layers is promoted by Cu sites, as reflected in the decrease of positive charge of Cu (Fig. 6D).
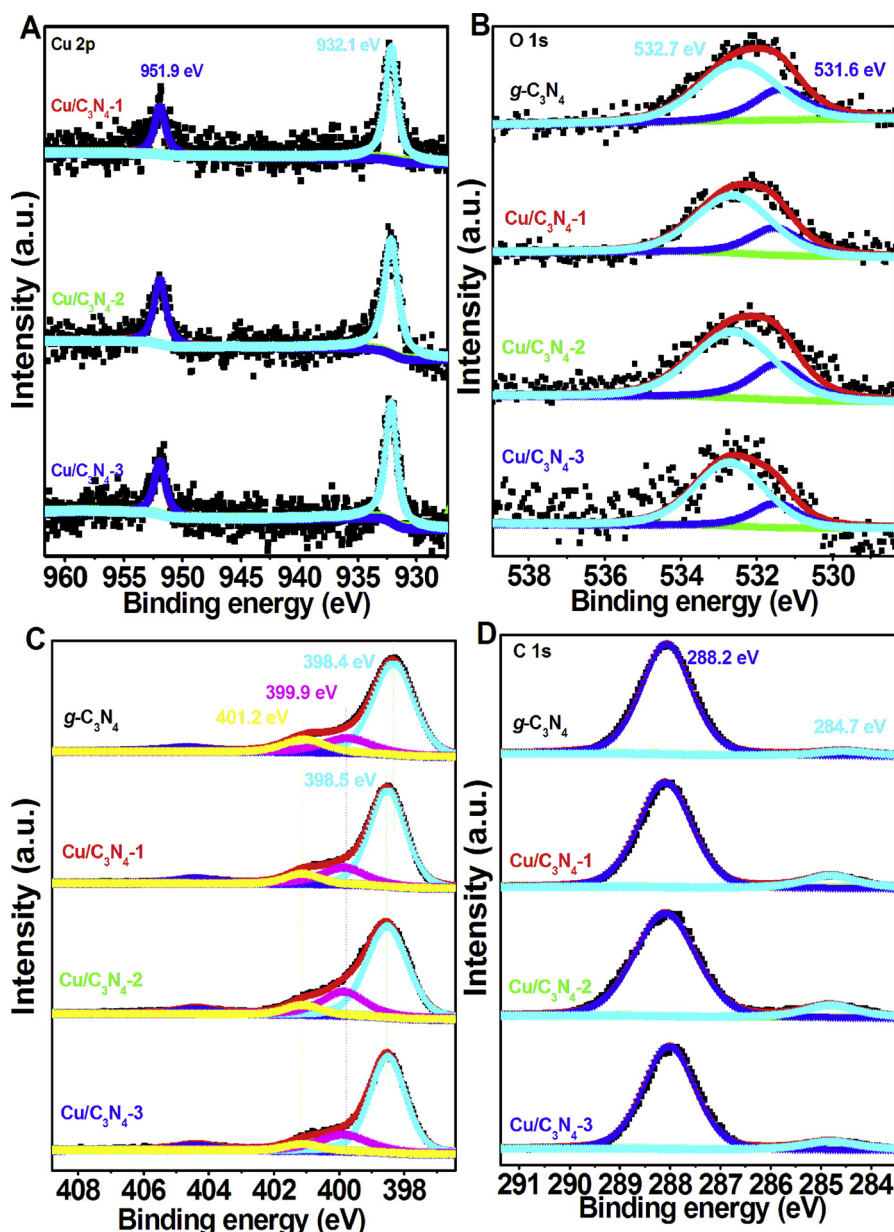
Fig. 2. XPS spectra of *g*-C₃N₄ and Cu/C₃N₄ samples, (A) Cu 2p, (B) O 1s, (C) N 1s, and (D) C 1s.

Fig. 3. FT-IR spectra of *g*-C₃N₄ and Cu/C₃N₄ samples.

3.4. Optical and electrical properties

From the above series characterizations of components and structure, it is seen that Cu^{2+} coordinates with sp^2-hybridized N atoms at vacancy sites of the conjugated tri-s-triazine nanosheet, which thus perfects π-delocalization structure of *g*-C₃N₄ and will improve its light absorption region and electronic structure. In Fig. 7A, it is seen that the light-absorption edge for *g*-C₃N₄ is 424 nm. However, for Cu/C₃N₄ samples, the absorption spectra demonstrate clearly a red shift with the strengthened light intensity, revealing that the as extended π-conjugated structure is conducive to light capturing due to Cu^{2+} co-ordination with sp^2-hybridized N at vacancy site of tri-s-triazine. Taking Cu/C₃N₄-3 as an example, the absorption edge expands to 468 nm with the enhanced absorption from UV to near NIR. On the basis of photon energy *vs.* $(\alpha h\nu)^{1/2}$, band gaps (E_g) is 2.73, 2.64, 2.54, and 2.41 eV corresponding successively to *g*-C₃N₄, Cu/C₃N₄-1, Cu/C₃N₄-2, and Cu/C₃N₄-3 samples (Fig. S2). The narrowed band gaps for Cu/C₃N₄ samples promote light absorption and photoelectron transition. Moreover, EPR curves of *g*-C₃N₄, and Cu/C₃N₄ are detected in Fig. 7B, and g values are
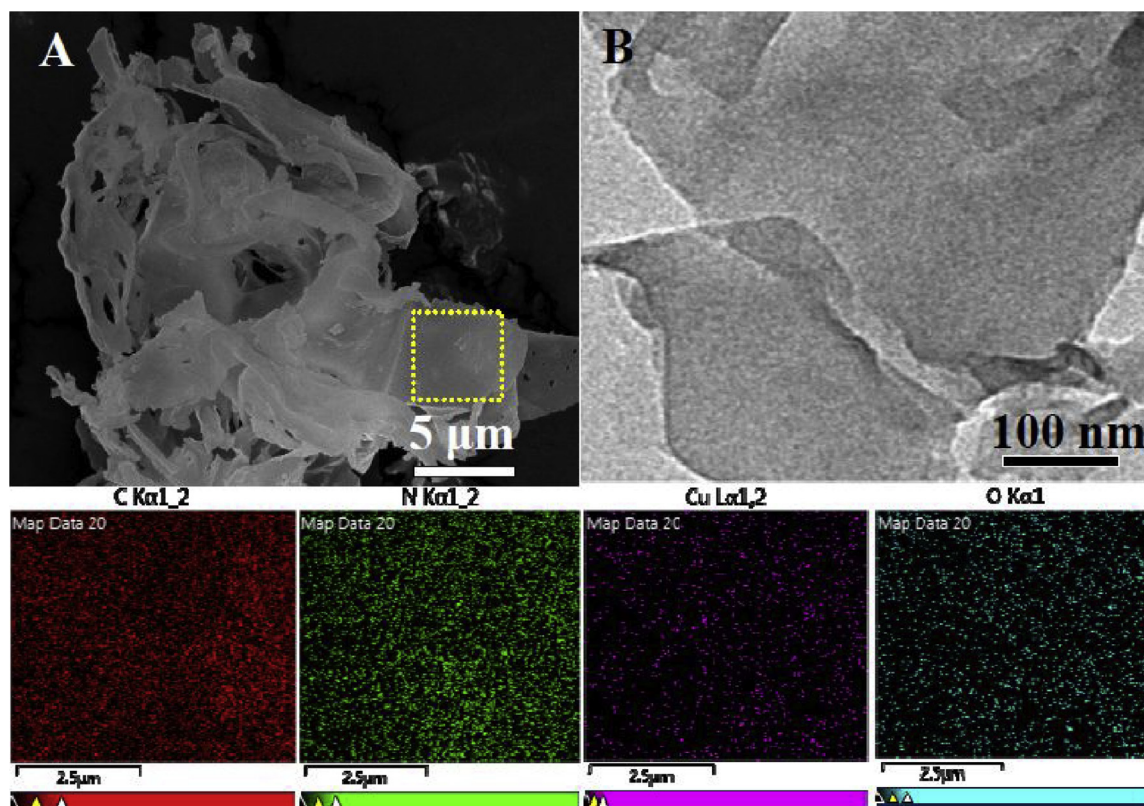
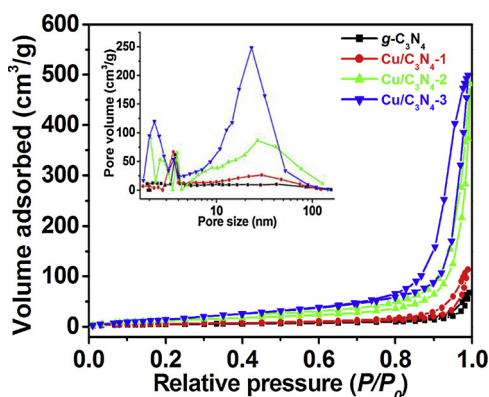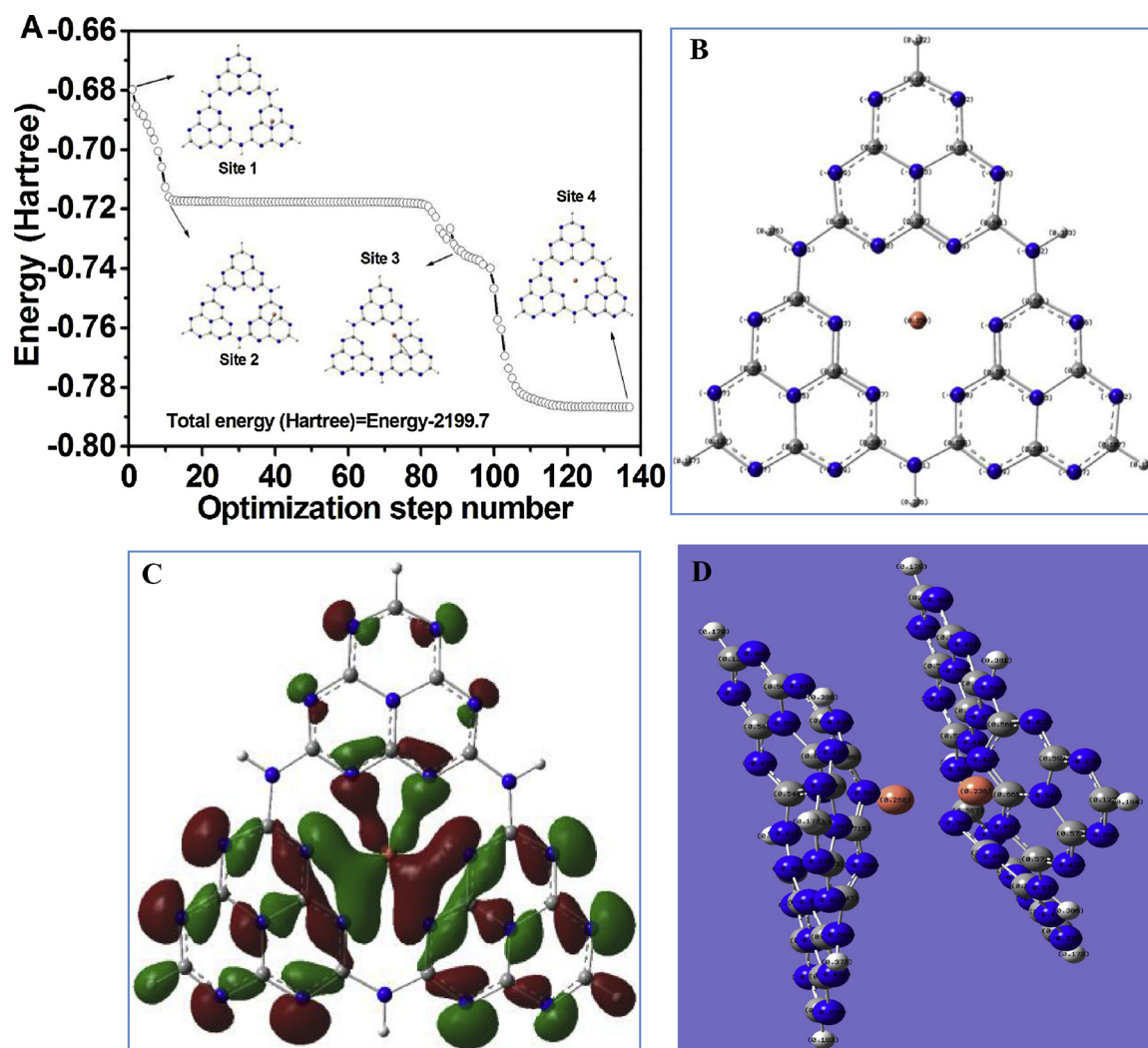**Fig. 4.** FESEM, TEM, and element mapping of Cu/C$_3$N$_4$-3.

Fig. 5. Nitrogen adsorption/desorption isothermal curves and the deduced pore properties of *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$ samples.

at 2.0000, which induces by lone electrons of the π-conjugated structure [53]. Cu/C$_3$N$_4$ samples exhibit the signals of EPR at 2.0000 with higher intensity, suggesting that the increased degree of delocalization [57]. In addition, time-resolved fluorescence spectra of *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$-3 samples were recorded by fitting with bi-exponential functions (Fig. 7C). Fast- and long-fluorescence decay spectra are essentially due to the non-radiative and radiative processes [53,58], respectively. Non-radiative step reflects the defect structure of semiconductor, and radiative step shows the recombination process of e$^-$ and h$^+$ [6,39,59]. In Fig. 7C, short lifetime (τ_1) for fast-fluorescence decay 1.2, 1.7, 2.2, and 2.5 ns, and the long lifetime (τ_2) for long-fluorescence decay is 5.8, 6.3, 6.8, and 7.3 ns, which corresponds to *g*-C$_3$N$_4$, Cu/C$_3$N$_4$-1, Cu/C$_3$N$_4$-2, and Cu/C$_3$N$_4$-3, respectively. The percent of the non-radiation step reduces with the extended short lifetime for Cu/C$_3$N$_4$-3 in comparison with that for *g*-C$_3$N$_4$, suggesting the decrease of defect structure for Cu/C$_3$N$_4$ as a result of coordination between Cu^{2+} 3d with N 2p$_z$ electron of

vacancy of tri-s-triazine nanosheet. Meanwhile, the extended π-conjugated structure boosts the charge transfer of Cu/C$_3$N$_4$, which presents as the extended-long lifetime and normal radiation percent. In the EIS-Nyquist characterization (Fig. 7D), the semicircle curves originate from charge transportation between electrode and electrolyte [60]. Cu/C$_3$N$_4$ samples demonstrate smaller electric-resistance compared with *g*-C$_3$N$_4$, stating clearly that Cu/C$_3$N$_4$ samples efficiently promotes electron transfer. Under light irradiation, photoelectron over sample transports into its back contact and interacts with electrolyte to produce photocurrent [61], as shown in the i-t patterns (Fig. 7E), obviously, the highest anodic photocurrent intensity is achieved on Cu/C$_3$N$_4$-3. When O$_2$ interacts with Cu/C$_3$N$_4$, photoelectron is preferentially trapped with O$_2$, which therefore impels h$^+$ diffusion on the surface of electrode, forming SPS signals. Accordingly, the signal intensity is proportional to the efficiency of charge transfer and utilization [62,63], and Cu/C$_3$N$_4$-3 reflects optimal efficiency of photo-irradiated charge transportation (Fig. 7F). As a result, photo-irradiated charge transfer over Cu/C$_3$N$_4$ samples will be preferentially transferred to the dissolved O$_2$ to evolve ROS in the aqueous oxygen system under light irradiation.

3.5. Photocatalytic performance

EPR was performed to examine active oxygen species, and DMPO was developed to test ˙OH and ˙O$_2^-$ by detecting the corresponding signals, respectively. In Fig. 8A, EPR patterns of DMPO-˙O$_2^-$ with peak intensity ratio of 1:1:1:1 are exhibited [64,65], and the much obvious DMPO-˙O$_2^-$ peaks are achieved for Cu/C$_3$N$_4$ samples, however, for *g*-C$_3$N$_4$, the peak intensity is relative weaker. Besides, ˙OH signals with the ratio of 1:2:2:1 are hardly tested for *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$ samples (Fig. 8B) [6,50,64]. Therefore, ˙O$_2^-$ can be photocatalytically yielded over *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$ samples, which is consistent with the CB and VB potentials of *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$. In Fig. S4, it is seen that CB potentials for *g*-C$_3$N$_4$, and Cu/C$_3$N$_4$ satisfy thermodynamic requirement from O$_2$ to ˙O$_2^-$, however VB potentials are not suitable for

Fig. 6. The optimization process of Cu/C$_3$N$_4$ geometry by Cu coordination with different site of conjugated tri-s-triazine (A), Mülliken charge distribution over monolayer Cu/C$_3$N$_4$ (B), the corresponding overlap of 2p$_z$ orbitals of N at vacancy sites and Cu^{2+} 3d orbitals (C), and Mülliken charge distribution between adjacent-layer Cu/C$_3$N$_4$ (D).

requirement of ˙OH evolution. In addition, the photocatalytic amount of ˙O$_2^-$ is tested by NBT transform method [66,67]. As shown in Fig. S5, absorption peak at 259 nm gradually declines in photoluminescence of NBT, indicating that NBT is consistently oxidized with O$_2^-$ over Cu/ C$_3$N$_4$-3 sample. On the basis of reaction molar ratio (n(NBT)/n (O$_2^-$) = 1:4), O$_2^-$ production is 3, 5, 9, and 13 µmol L^{-1} h^{-1} over g-C$_3$N$_4$, Cu/C$_3$N$_4$-1, Cu/C$_3$N$_4$-2, and Cu/C$_3$N$_4$-3 (Fig. 8C), respectively, and the optimal photocatalytic efficiency for O$_2^-$ evolution is completed over Cu/C$_3$N$_4$-3. In Fig. 8D, effect of irradiation time on O$_2^-$ efficiency with g-C$_3$N$_4$ and Cu/C$_3$N$_4$ sample as photocatalyst is displayed, and continuing O$_2^-$ yield is observed with no decline of evolution efficiency, nevertheless, the performance trend diagram vs. time is obviously different over g-C$_3$N$_4$ and Cu/C$_3$N$_4$ samples. After 120 min reaction, O$_2^-$ evolution efficiency increases slowly over g-C$_3$N$_4$, while the photocatalytic efficiency maintains high rates for Cu/C$_3$N$_4$ samples, specially for Cu/C$_3$N$_4$-3, the fast increase of O$_2^-$ efficiency can be obtained. The results of the enhanced photocatalytic activity for O$_2^-$ evolution over Cu/C$_3$N$_4$ can be achieved due to the formation of extended π-conjugated structure by coordinating Cu^{2+} with N 2p$_z$ of tri-s-triazine nanosheet in combination with the above series characterizations.

Besides, Cu/C$_3$N$_4$ samples display high activity for H$_2$O$_2$ evolution, and the results are shown in Fig. 8E. H$_2$O$_2$ evolution efficiency over Cu/ C$_3$N$_4$ samples is greatly higher than that over g-C$_3$N$_4$ (200 µmol L^{-1} h^{-1}). For Cu/C$_3$N$_4$ samples, H$_2$O$_2$ evolution efficiency over Cu/ C$_3$N$_4$-1, Cu/C$_3$N$_4$-2, and Cu/C$_3$N$_4$-3 is 389, 460, and 550 µmol L^{-1} h^{-1}. Cu/C$_3$N$_4$-3 sample possesses the optimal efficiency which is 2.75 times that of g-C$_3$N$_4$ under light irradiation with same wavelength. These photocatalytic performances state clearly that the coordination of Cu^{2+} with N 2p$_z$ of vacancy structure of g-C$_3$N$_4$ promotes H$_2$O$_2$ photosynthesis. In Fig. S10, influence of illumination time on H$_2$O$_2$ efficiency over all samples is also investigated, and sustainable H$_2$O$_2$ yield is achieved with no decline, nevertheless, the efficiency-trend diagram vs. time is clearly diversity over g-C$_3$N$_4$ and Cu/C$_3$N$_4$ samples. In the 120 min of photocatalytic reaction process, H$_2$O$_2$ production efficiency enhances mildly over g-C$_3$N$_4$, while the efficiency demonstrates the high rates for Cu/C$_3$N$_4$ samples, indicating the sustainable evolution capability of H$_2$O$_2$ over the extended π-conjugated structure. Additionally, excitation-wavelength effect on H$_2$O$_2$ efficiency over Cu/C$_3$N$_4$-3 is also probed, Fig. 8F demonstrates the continuous H$_2$O$_2$ evolution with 240 and 75 µmol L^{-1} h^{-1} over Cu/C$_3$N$_4$-3 under visible light (560 nm) and near infrared light (≥780 nm) irradiation, respectively. On the other hand, no H$_2$O$_2$ was observed when g-C$_3$N$_4$ was used as photocatalyst (Fig. S6). Moreover, H$_2$O$_2$ efficiency over Cu/C$_3$N$_4$-3 is coincident with its absorption spectrum. Therefore, the Cu/C$_3$N$_4$-3 performs well in the visible and near infrared region, promising the more efficient utilization
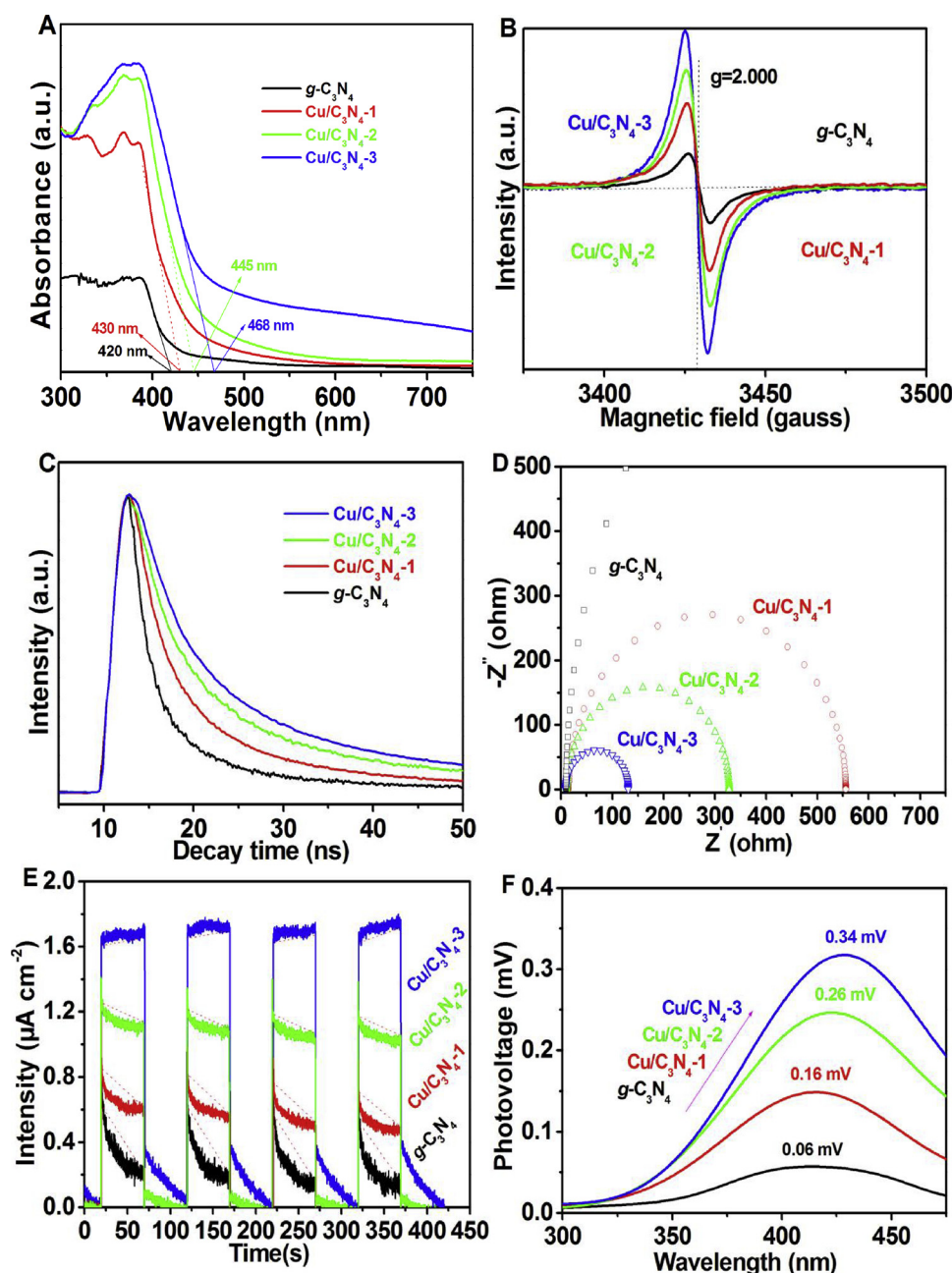
Fig. 7. UV–vis spectra (A), EPR patterns (B), time-resolved fluorescence spectra (C), electrochemical impedance spectra (D), transient photocurrent response (E), and surface photovoltage spectra (F) of g-C_3N_4 and Cu/C_3N_4 samples.
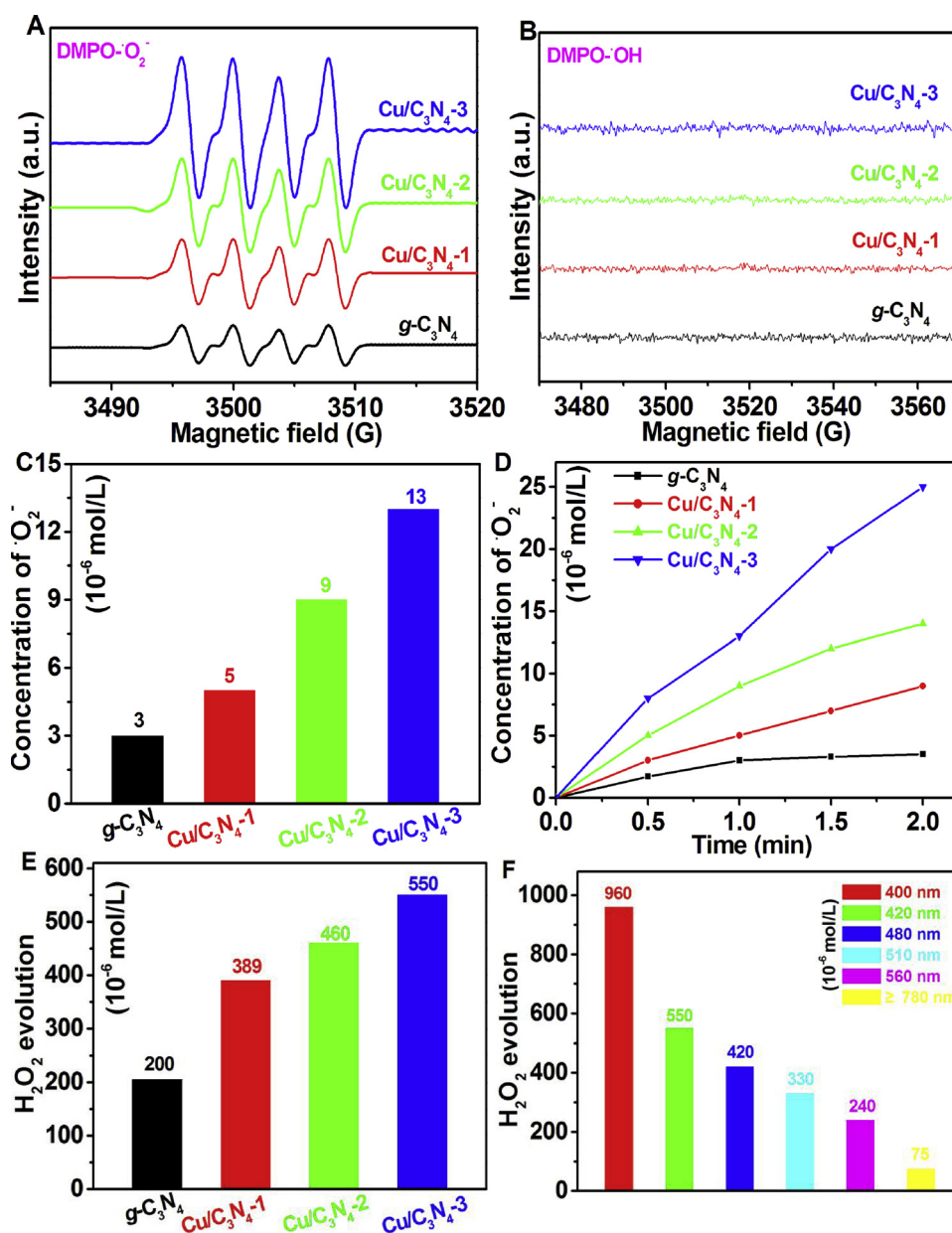
of long-wavelength solar energy in comparison with g-C_3N_4. In connection with the O_2^- evolution efficiency, it is concluded that the improved π-conjugated structure of Cu/C_3N_4 with the optimized electron structure promotes the efficiently sustainable evolution of O_2^- and H_2O_2.

In consideration of importance of reactive oxygen species in the environment, Cu/C_3N_4 samples were as well performed to decontaminate NO, and HCHO pollutants, and the results are displayed in Fig. 9. Only 52 ppm of HCHO was eliminated in the presence of g-C_3N_4, which is due to the severe recombination of photo-induced e^- and h^+. After coordinating N 2p lone electrons of vacancy of tri-s-triazine with vacant orbits of Cu^{2+}, elimination efficiency of HCHO greatly enhances, specifically, HCHO content declines from 200 ppm to 79, 53, and 29 for Cu/C_3N_4-1, Cu/C_3N_4-2, Cu/C_3N_4-3, respectively (Fig. 9A). Correspondingly, CO_2 content increases to 77, 178, 216, and 251 ppm for g-C_3N_4, Cu/C_3N_4-1, Cu/C_3N_4-2, and, Cu/C_3N_4-3, respectively (Fig. 9B).

Moreover, Cu/C_3N_4 samples demonstrate high stability in the recycle tests for HCHO elimination (Fig. S7). In the photocatalytic removal of NO, Cu/C_3N_4 samples also display better catalytic efficiency than g-C_3N_4, i.e., 30.2 (g-C_3N_4), 44.3 (Cu/C_3N_4-1), 61.2 (Cu/C_3N_4-2), and 108 $\mu mol\,L^{-1}\,h^{-1}$ (Cu/C_3N_4-3), and the removal efficiency of NO over the optimal Cu/C_3N_4 is 3.57 times of that over g-C_3N_4. Previous reports confirm that elimination efficiency of HCHO and NO over g-C_3N_4 is closely related to the photocatalytic yield of ROS [39], which confirms the great importance of ROS over Cu/C_3N_4 for environmental purification.

Whereafter, the photocatalytic principles of O_2^-, and H_2O_2 production over g-C_3N_4, and Cu/C_3N_4 are probed. In Fig. 10, N_2 (99.999%) was used to consume the dissolved O_2 in the photocatalytic system of ROS evolution. It is seen that H_2O_2 yield for g-C_3N_4 and Cu/C_3N_4-3 can not be completed vanished, stating clearly that H_2O_2 production is not merely by photocatalytically reducing the dissolved O_2 with photo-

Fig. 8. EPR spectra of DMPO-$\cdot O_2^-$ in the methanol dispersion solution (A), DMPO-$\cdot OH$ in aqueous dispersion (B) over g-C_3N_4, and Cu/C_3N_4 samples, yield efficiency of $\cdot O_2^-$ (C), and H_2O_2 (E), time- and wavelength-dependent effects on the efficiency of $\cdot O_2^-$ (D), and H_2O_2 (F), respectively.

induced e^-. A small quantity of H_2O_2 is produced under N_2 bubbling for g-C_3N_4, and Cu/C_3N_4-3, because the photo-induced h^+ of g-C_3N_4 and Cu/C_3N_4 oxidizes H_2O into O_2 for compensating the dissolved oxygen, and 12.7 μmol h^{-1} for O_2 evolution over Cu/C_3N_4-3 has been achieved in the presence of AgNO$_3$. H_2O_2 evolution efficiency for Cu/C_3N_4-3 is greatly higher than that for g-C_3N_4, indicating the effective utilization of h^+ over Cu/C_3N_4-3. The results also reveal that the efficient charge transfer is achieved on Cu/C_3N_4-3. Moreover, the improved hydrophilicity of Cu/C_3N_4-3 favors H_2O adsorption and oxidation, which is also confirmed by hydrophilicity test results in the Fig. S8. It is seen that the H_2O contact angle decreases from 43.3 (g-C_3N_4) to 21.5 (Cu/C_3N_4-3). When H_2PtCl_6 is utilized to delete photo-induced e^-, H_2O_2 was not detected for g-C_3N_4, and Cu/C_3N_4-3. In photocatalytic H_2O_2 evolution process, H_2O_2 is achieved by O_2^- reduction with e^-. Due to coordinating Cu^{2+} with N 2p_z of vacancy of tri-s-triazine nanosheet, the charge distribution is homogenized, and the electronegativity difference between C and N is decreased over the extended π-conjugated structure of Cu/C_3N_4, thus greatly promoting the effective

transfer of photo-induced charge carriers. In the visible-light irradiation process, photo-induced e- conveniently reacts with O_2, which produces O_2^-. Afterwards, the photocatalytically produced O_2^- further interacts with e^- and H^+, as a result producing H_2O_2. The detailed photosynthesis process of ROS is displayed in the inset of Fig. 10.

4. Conclusion

In summary, efficient photocatalytic system for yielding reactive oxygen species over the extended π-delocalization Cu/C_3N_4 photocatalysts have been designed by coordinating the vacancy of tri-s-triazine polymer with Cu 3d orbit. Cu/C_3N_4 photocatalysts exhibit great performance for evolving O_2^-, and H_2O_2. High efficiency over Cu/C_3N_4 principally arises from the facilitating role of the extended π-delocalization structure. The extended π-delocalization structure of Cu/C_3N_4 results in i) the strengthened harvesting capability from UV-NIR, ii) the efficient charge transfer ability from intrinsic material to O_2 molecular at sites of C (in C_3-N) and Cu. In the removal process of HCHO, and NO,
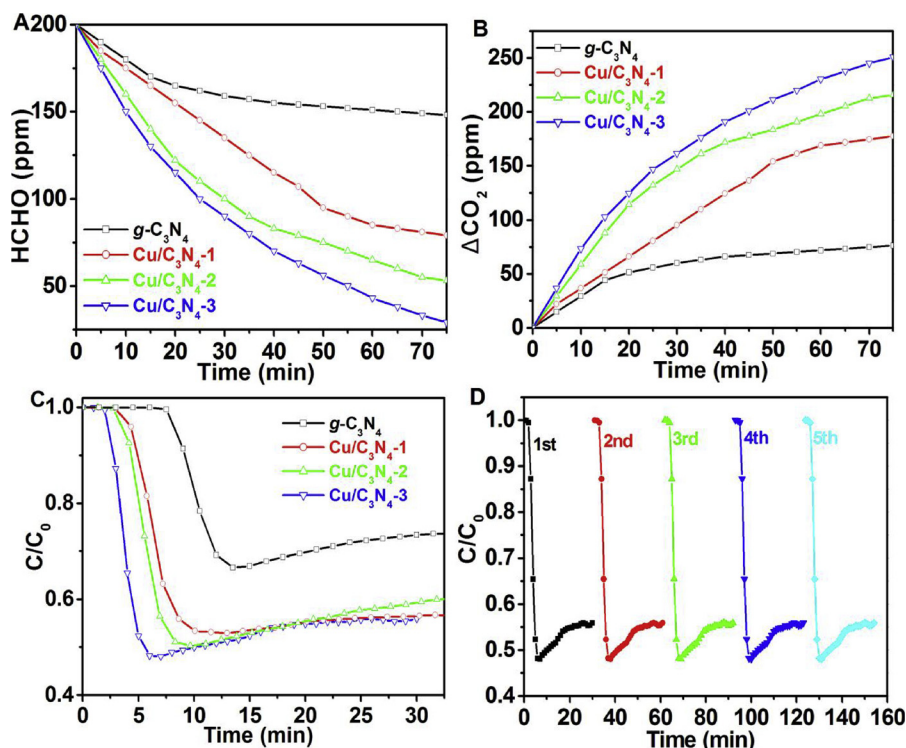
Fig. 9. Elimination efficiency for HCHO (A), and NO (C), the conversion performance from HCHO to CO$_2$ (B), and the recycles test for NO elimination (D) over g-C$_3$N$_4$ and Cu/C$_3$N$_4$ samples.

Fig. 10. The effect of scavengers (H$_2$PtCl$_6$, KI, IPA, N$_2$ for e$^-$, h$^+$, $\cdot$OH, O$_2$, respectively) on H$_2$O$_2$ yield over Cu/C$_3$N$_4$-3, and the corresponding mechanism for photocatalytic evolution of $\cdot$O$_2^-$ and H$_2$O$_2$.

Cu/C$_3$N$_4$ photocatalysts demonstrate high and sustainable removal efficiency. The highly active photocatalytic system over the extended π-delocalization g-C$_3$N$_4$ photocatalysts constructed by the convenient and low cost strategy demonstrates a promising application prospect for sustainable evolution and utilization of solar fuel.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.03.014.

References

[1] S.O. Ganiyu, M.H. Zhou, C.A. Martinez-Huitle, Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment, Appl. Catal. B: Environ. 235 (2018) 103–129.

[2] P. Ganguly, C. Byme, A. Breen, S.C. Pillai, Antimicrobial activity of photocatalysts: fundamentals, mechanisms, kinetics and recent advances, Appl. Catal. B: Environ. 225 (2018) 51–75.

[3] Y. Nosaka, A.Y. Nosaka, Generation and detection of reactive oxygen species in photocatalysis, Chem. Rev. 117 (2017) 11302–11336.

[4] T. Bak, J. Nowotny, N.J. Sucher, E. Wachsman, Effect of crystal imperfections on reactivity and photoreactivity of TiO$_2$ (Rutile) with oxygen, water, and bacteria, J. Phys. Chem. C 115 (2011) 15711–15738.

[5] N. Waiskopf, Y. Ben-Shahar, M. Galchenko, I. Carmel, G. Moshitzky, H. Soreq, U. Banin, Photocatalytic reactive oxygen species formation by semiconductor-metal hybrid nanoparticles. Toward light-induced modulation of biological processes, Nano Lett. 16 (2016) 4266–4273.

[6] C.B. Xiong, S.J. Jiang, S.Q. Song, X. Wu, J.H. Li, Z.G. Le, Solid-solution-like o-C$_3$N$_4$/ Ag$_2$SO$_4$ nanocomposite as a direct Z-scheme photocatalytic system for photosynthesis of active oxygen species, ACS Sustain. Chem. Eng. 6 (2018) 10905–10913.

[7] S.Q. Huang, Y.G. Xu, Q.Q. Liu, T. Zhou, Y. Zhao, L.Q. Jing, H. Xu, H.M. Li, Enhancing reactive oxygen species generation and photocatalytic performance via adding oxygen reduction reaction catalysts into the photocatalysts, Appl. Catal. B: Environ. 218 (2017) 174–185.

[8] P. Chen, F.L. Wang, Z.F. Chen, Q.X. Zhang, Y.H. Su, L.Z. Shen, K. Yao, Y. Liu, Z.W. Cai, W.Y. Lv, G.G. Liu, Study on the photocatalytic mechanism and detoxity of gemfibrozil by a sunlight-driven TiO$_2$/carbon dots photocatalyst: The significant roles of reactive oxygen species, Appl. Catal. B: Environ. 204 (2017) 250–259.

[9] H.X. Zhao, X.Y. Chen, X.T. Li, C. Shen, B.C. Qu, J.S. Gao, J.W. Chen, X. Quan, Photoinduced formation of reactive oxygen species and electrons from metal oxide-silica nanocomposite: an EPR spin-trapping study, Appl. Surf. Sci. 416 (2017) 281–287.

[10] Y.Y. Qin, H. Li, J. Lu, Y.S. Yan, Z.Y. Lu, X.L. Liu, Enhanced photocatalytic performance of MoS₂ modified by AgVO₃ from improved generation of reactive oxygen species, Chin. J. Catal. 39 (2018) 1470–1483.

[11] J.Y. Gong, C.S. Lee, E.J. Kim, J.H. Kim, W. Lee, Y.S. Chang, Self-generation of reactive oxygen species on crystalline AgBiO₃ for the oxidative remediation of organic pollutants, ACS Appl. Mater. Interfaces 9 (2017) 28426–28432.

[12] S.Q. Song, A.Y. Meng, S.J. Jiang, B. Cheng, Three-dimensional hollow graphene efficiently promotes electron transfer of Ag₃PO₄ for photocatalytically eliminating phenol, Appl. Surf. Sci. 442 (2018) 224–231.

[13] Y. Zheng, Z.H. Yu, H.H. Ou, A.M. Asiri, Y.L. Chen, X.C. Wang, Black phosphorous and polymeric carbon nitride heterostructure for photoinduced molecular oxygen activation, Adv. Funct. Mater. 28 (2018) 1705407.

[14] J. Li, L.J. Cai, J. Shang, Y. Yu, L.Z. Zhang, Giant enhancement of internal electric field boosting bulk charge separation for photocatalysis, Adv. Mater. 28 (2016) 4059–4064.

[15] M.R. Hoffmannn, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[16] H.W. Huang, S.C. Tu, C. Zeng, T.R. Zhang, A.H. Reshak, Y.H. Zhang, Macroscopic polarization enhancement promoting photo- and piezoelectric-induced charge separation and molecular oxygen activation, Angew. Chem. Int. Ed. 56 (2017) 11860–11864.

[17] Z.J. Li, Y.B. Luan, Y. Qu, L.Q. Jing, Modification strategies with inorganic acids for efficient photocatalysts by promoting the adsorption of O₂, ACS Appl. Mater. Interfaces 7 (2015) 22727–22740.

[18] J.W. Fu, J.G. Yu, C.J. Jiang, B. Cheng, g-C₃N₄-based heterostructured photocatalysts, Adv. Energy Mater. 8 (2018) 1701503.

[19] S.W. Cao, J.X. Low, J.G. Yu, M. Jaroniec, Polymeric photocatalysts based on graphitic carbon nitride, Adv. Mater. 27 (2015) 2150–2176.

[20] G. Mamba, A.K. Mishra, Graphitic carbon nitride (g-C₃N₄) nanocomposites: a new and exciting generation of visible light driven photocatalysts for environmental pollution remediation, Appl. Catal. B: Environ. 198 (2016) 347–377.

[21] X.L. Liu, P. Wang, H.S. Zhai, Q.Q. Zhang, B.B. Huang, Z.Y. Wang, Y.Y. Liu, Y. Dai, X.Y. Qin, X.Y. Zhang, Synthesis of synergetic phosphorus and cyano groups (CN) modified g-C₃N₄ for enhanced photocatalytic H₂ production and CO₂ reduction under visible light irradiation, Appl. Catal. B: Environ. 232 (2018) 521–530.

[22] H.L. Li, F.P. Li, Z.Y. Wang, Y.C. Jiao, Y.Y. Liu, P. Wang, X.Y. Zhang, X.Y. Qin, B.B. Huang, Fabrication of carbon bridged g-C₃N₄ through supramolecular self-assembly for enhanced photocatalytic hydrogen evolution, Appl. Catal. B: Environ. 229 (2018) 114–120.

[23] W.J. Wang, H.F. Cheng, B.B. Huang, X.L. Liu, X.Y. Qin, X.Y. Zhang, Y. Dai, Hydrothermal synthesis of C₃N₄/BiOIO₃ heterostructures with enhanced photocatalytic properties, J. Colloid Interface Sci. 442 (2015) 97–102.

[24] Q.M. Zheng, D.P. Durkin, J.E. Elenewski, Y.X. Sun, N.A. Banek, L.K. Hua, H.N. Chen, M.J. Wagner, W. Zhang, D.M. Shuai, Visible-light-responsive graphitic carbon nitride: rational design and photocatalytic applications for water treatment, Environ. Sci. Technol. 50 (2016) 12938–12948.

[25] L.L. Feng, F. He, G.X. Yang, S.L. Gai, Y.L. Dai, C.X. Li, P.P. Yang, NIR—driven graphitic-phase carbon nitride nanosheets for efficient bioimaging and photodynamic therapy, J. Mater. Chem. B 4 (2016) 8000–8008.

[26] S.F. Kang, L. Zhang, C.C. Yin, Y.G. Li, L.F. Cui, Y.G. Wang, Fast flash frozen synthesis of holey few-layer g-C₃N₄ with high enhancement of photocatalytic reactive oxygen species evolution under visible light irradiation, Appl. Catal. B: Environ. 211 (2017) 266–274.

[27] J.D. Xiao, J. Rabeah, J. Yang, Y.B. Xie, H.B. Cao, A. Bruckner, Fast electron transfer and (OH)-O-center dot formation: key features for high activity in visible-light-driven ozonation with C₃N4 catalysts, ACS Catal. 7 (2017) 6198–6206.

[28] D.H. Xia, W.J. Wang, R. Yin, Z.F. Jiang, T.C. An, G.Y. Li, H.J. Zhao, P.K. Wong, Enhanced photocatalytic inactivation of Escherichia coli by a novel Z-scheme g-C₃N₄/m-Bi₂O₄ hybrid photocatalyst under visible light: the role of reactive oxygen species, Appl. Catal. B: Environ. 214 (2017) 23–33.

[29] J.D. Xiao, Q.Z. Han, Y.B. Xie, J. Yang, Q.Z. Su, Y. Chen, H.B. Cao, Is C₃N₄ chemically stable toward reactive oxygen species in sunlight-driven water treatment? Environ. Sci. Technol. 51 (2017) 13380–13387.

[30] W.D. Oh, L.W. Lok, A. Veksha, A. Giannis, T.T. Lim, Enhanced photocatalytic degradation of bisphenol A with Ag-decorated S-doped g-C₃N₄ under solar irradiation: Performance and mechanistic studies, Chem. Eng. J. 333 (2018) 739–749.

[31] L.P. Yang, G.H. Dong, D.L. Jacobs, Y.H. Wang, L. Zang, C.Y. Wang, Two-channel photocatalytic production of H₂O₂ over g-C₃N₄ nanosheets modified with perylene imides, J. Catal. 352 (2017) 274–281.

[32] S. Zhao, X. Zhao, S.X. Ouyang, Y.F. Zhu, Polyoxometalates covalently combined with graphitic carbon nitride for photocatalytic hydrogen peroxide production, Catal. Sci. Technol. 8 (2018) 1686–1695.

[33] J. Wang, Z. Yang, W.Q. Yao, X.X. Gao, D.P. Tao, Defects modified in the exfoliation of g-C₃N₄ nanosheets via a self-assembly process for improved hydrogen evolution performance, Appl. Catal. B: Environ. 238 (2018) 629–637.

[34] L. Jing, R.X. Zhu, D.L. Phillips, J.C. Yu, Effective prevention of charge trapping in graphitic carbon nitride with nanosized red phosphorus modification for superior photo(electro)catalysis, Adv. Funct. Mater. 27 (2017) 1703484.

[35] J. Xu, L.W. Zhang, R. Shi, Y.F. Zhu, Chemical exfoliation of graphitic carbon nitride for efficient heterogeneous photocatalysis, J. Mater. Chem. A 1 (2013) 14766–14772.

[36] Y.Y. Kang, Y.Q. Yang, L.C. Yin, X.D. Kang, L.Z. Wang, G. Liu, H.M. Cheng, Selective breaking of hydrogen bonds of layered carbon nitride for visible light photocatalysis, Adv. Mater. 28 (2016) 6471–6477.

[37] P. Niu, L.L. Zhang, G. Liu, H.M. Cheng, Graphene-like carbon nitride nanosheets for improved photocatalytic activities, Adv. Funct. Mater. 22 (2012) 4763–4770.

[38] S.J. Jiang, C.B. Xiong, S.Q. Song, B. Cheng, Plasmonic graphene-like Au/C₃N₄ nanosheets with barrier-free interface for photocatalytically sustainable evolution of active oxygen species, ACS Sustain. Chem. Eng. 7 (2019) 2018–2026, https://doi.org/10.1021/acssuschemeng.8b04338.

[39] S.Q. Song, C.H. Lu, X. Wu, S.J. Jiang, C.Z. Sun, Z.G. Le, Strong base g-C₃N₄ with perfect structure for photocatalytically eliminating formaldehyde under visible-light irradiation, Appl. Catal. B: Environ. 227 (2018) 145–152.

[40] S.X. Min, G.X. Lu, Enhanced electron transfer from the excited Eosin Y to mpg-C₃N₄ for highly efficient hydrogen evolution under 550 nm irradiation, J. Phys. Chem. C 116 (2012) 19644–19652.

[41] Z. Li, C. Kong, G.X. Lu, Visible photocatalytic water splitting and photocatalytic two-electron oxygen formation over Cu- and Fe-doped g-C₃N₄, J. Phys. Chem. C 120 (2016) 56–63.

[42] Z. Li, Y.Q. Wu, G.X. Lu, Highly efficient hydrogen evolution over Co(OH)₂ nanoparticles modified g-C₃N₄ co-sensitized by Eosin Y and Rose bengal under visible light irradiation, Appl. Catal. B: Environ. 188 (2016) 56–64.

[43] X. Wu, S.J. Jiang, S.Q. Song, C.Z. Sun, Constructing effective photocatalytic purification system with P-introduced g-C₃N₄ for elimination of UO₂²⁺, Appl. Surf. Sci. 430 (2018) 371–379.

[44] X. Wu, C.H. Lu, J.J. Liu, S.Q. Song, C.Z. Sun, Constructing efficient solar light photocatalytic system with Ag-introduced carbon nitride for organic pollutant elimination, Appl. Catal. B: Environ. 217 (2017) 232–240.

[45] W.N. Xing, G. Chen, C.M. Li, Z.H. Han, Y.D. Hu, Q.Q. Meng, Doping effect of non-metal group in porous ultrathin g-C₃N₄ nanosheets towards synergistically improved photocatalytic hydrogen evolution, Nanoscale 10 (2018) 5239–5245.

[46] G.G. Zhang, X.C. Wang, A facile synthesis of covalent carbon nitride photocatalysts by co-polymerization of urea and phenylurea for hydrogen evolution, J. Catal. 307 (2013) 246–253.

[47] Y. Jiao, Y. Zheng, P. Chen, M. Jaroniec, S.Z. Qiao, Molecular scaffolding strategy with synergistic active centers to facilitate electrocatalytic CO₂ reduction to hydrocarbon/alcohol, J. Am. Chem. Soc. 139 (2017) 18093–18100.

[48] W. Iqbal, B.C. Qiu, Q.H. Zhu, M.Y. Xing, J.L. Zhang, Self-modified breaking hydrogen bonds to highly crystalline graphitic carbon nitrides nanosheets for drastically enhanced hydrogen production, Appl. Catal. B: Environ. 232 (2018) 306–313.

[49] A. Cohen, Y.Z. Yang, Q.L. Yan, A. Shlomovich, N. Petrutik, L. Burstein, S.P. Pang, M. Gozin, Highly thermostable and insensitive energetic hybrid coodiation polymers based on graphene oxide-Cu(II) complex, Chem. Mater. 28 (2016) 6118–6126.

[50] P.F. Xia, B.C. Zhu, B. Cheng, J.G. Yu, J.S. Xu, 2D/2D g-C₃N₄/MnO₂ nanocomposite as a direct Z-scheme photocatalyst for enhanced photocatalytic activity, ACS Sustain. Chem. Eng. 6 (2018) 965–973.

[51] T. Zhang, D. Zhang, X.H. Han, T. Dong, X.W. Guo, C.S. Song, R. Si, W. Liu, Y.F. Liu, Z.K. Zhao, Preassembly strategy to fabricate porous hollow carbonitride spheres inlaid with single Cu-N3 sites for selective oxidation of benzene to phenol, J. Am. Chem. Soc. 140 (2018) 16936–16940.

[52] Y.Y. Ni, Z.Y. Chen, F.T. Kong, Y. Qiao, A.G. Kong, Y.K. Shan, Space-confined synthesis of multilayer Cu-N-doped graphene nanosheets for efficient oxygen electroreduction, Dalton Trans. 46 (2017) 8586–8592.

[53] P.F. Xia, M.J. Liu, B. Cheng, J.G. Yu, L.Y. Zhang, Dopamine modified g-C₃N₄ and its enhanced visible-light photocatalytic H₂-production activity, ACS Sustain. Chem. Eng. 6 (2018) 8945–8953.

[54] M. Kruk, M. Jaroniec, Gas adsorption characterization of ordered organic-inorganic nanocomposite materials, Chem. Mater. 13 (2001) 3169–3183.

[55] T. Moriuchi, T. Hirao, Design and redox function of conjugated complexes with polyanilines or quinonediimines, Acc. Chem. Res. 45 (2012) 347–360.

[56] N. Wang, J. Wang, J.H. Hu, X.Q. Lu, J. Sun, F. Shi, Z.H. Liu, Z.B. Lei, R.B. Jiang, Design of palladium-doped g-C₃N₄ for enhanced photocatalytic activity toward hydrogen evolution reaction, ACS Appl. Energy Mater. 1 (2018) 2866–2873.

[57] J.S. Zhang, M.W. Zhang, S. Liu, X.Z. Fu, X.C. Wang, Molecular doping of carbon nitride photocatalysts with tunable bandgap and enhanced activity, J. Catal. 310 (2014) 24–30.

[58] S.W. Cao, O. Huang, B.C. Zhu, J.G. Yu, Trace-level phosphorus and sodium co-doping of g-C₃N₄ for enhanced photocatalytic H₂ production, J. Power Sources 351 (2017) 151–159.

[59] K. Das, S.N. Sharma, M. Kumar, S.K. De, Morphology dependent luminescence properties of Co doped TiO₂ nanostructures, J. Phys. Chem. C 113 (2009) 14783–14792.

[60] D.P. Guo, S.Q. Xiao, K. Fan, J.G. Yu, Hierarchical TiO₂ submicrorods improve the photovoltaic performance of dye-sensitized solar cells, ACS Sustain. Chem. Eng. 5 (2017) 1315–1321.

[61] Q.J. Xiang, J.G. Yu, M. Jaroniec, Preparation and enhanced visible-light photocatalytic H₂-production activity of graphene/C₃N₄ composites, J. Phys. Chem. C 115 (2011) 7355–7363.

[62] X.L. Zhang, X.X. Zhang, J.D. Li, J.H. Sun, J. Bian, J.S. Wang, Y. Qu, R. Yan, C.L. Qin, L.Q. Jing, Exceptional visible-light activities of g-C₃N₄ nanosheets dependent on the unexpected synergistic effects of prolonging charge lifetime and catalyzing H₂ evolution with H₂O, Appl. Catal. B: Environ. 237 (2018) 50–58.

[63] J.S. Wang, C.L. Qin, H.J. Wang, M.N. Chu, A. Zada, X.L. Zhang, J.D. Li, F. Raziq, Y. Qu, L.Q. Jing, Exceptional photocatalytic activities for CO₂ conversion on Al-O bridged g-C₃N₄/α-Fe₂O₃ z-scheme nanocomposites and mechanism insight with isotopes, Appl. Catal. B: Environ. 221 (2018) 459–466.

[64] J.J. Kong, Z.B. Rui, H.B. Ji, Carbon nitride polymer sensitization and nitrogen doping of SrTiO₃/TiO₂ nanotube heterostructure toward high visible light photocatalytic performance, Ind. Eng. Chem. Res. 56 (2017) 9999–10008.

[65] W.J. Yang, Y.F. Zhu, F. You, L. Yan, Y.J. Ma, C.Y. Lu, P.Q. Gao, Q. Hao, W.L. Li, Insights into the surface-defect dependence of molecular oxygen activation over birnessite-type MnO₂, Appl. Catal. B: Environ. 233 (2018) 184–193.

[66] S.J. Liu, F.T. Li, Y.L. Li, Y.J. Hao, X.J. Wang, B. Li, R.H. Liu, Fabrication of ternary g-C₃N₄/Al₂O₃/ZnO heterojunctions based on cascade electron transfer toward molecular oxygen activation, Appl. Catal. B: Environ. 212 (2018) 115–128.

[67] V.L. Prasanna, R. Vijayaraghavan, Insight into the mechanism of antibacterial activity of ZnO: surface defects mediated reactive oxygen species even in the dark, Langmuir 31 (2015) 9155–9162.